

Polytechnic UNIVERSITY

FINAL REPORT

TO

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

AFOSR GRANT # F49620-93-1-~~0636~~ ⁰⁶⁰³

FIBER OPTIC INFRARED SPECTROSCOPY FOR "SMART" PROCESSING

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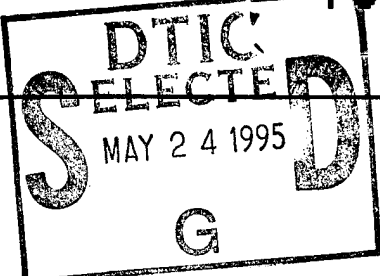
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13. ABSTRACT (Maximum 200 words) This is the final report on AFOSR #F49620-93-1-0603 entitled: "Fiber Optic Infrared Spectroscopy for "Smart" Processing". The report is divided into six sections. An Introductory paragraph contains a brief description of the background and the objectives. In-situ real time monitoring of chemical and physical changes during processing of reactive materials, polymer-forming and non polymer-forming alike, is of crucial importance to scientists and engineers engaged in efforts to optimize processes and products in various industries, from chemical and pharmaceutical to electronic and aerospace. Information collected in-situ by sensors is transmitted in real time to the process computer whose task is to control the system parameters by taking corrective actions without the need to examine the output streams and thus to guide the process along an optimum path. The principal elements of an in-situ process control loop are the signal source, the transmission line, the sensor and the detector. It is clearly desirable to operate a monitoring setup in the remote mode which enables one to continuously measure changes in chemical and physical properties as they occur during processing in difficult to access places, such as dies, molds, reactors or autoclaves, which operate in the presence of various				
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This is the final report on AFOSR Grant #F49620-93-1-0636 entitled: "Fiber Optic Infrared Spectroscopy for "Smart" Processing". The report is divided into six sections. An introductory paragraph contains a brief description of the background and the objectives. Experimental setups for remote near-infrared (NIR) and mid-infrared (MIR) spectroscopy are described in sections 2 and 3, respectively. Examples of typical results generated in our laboratory are given in section 4. Publications based entirely or in part upon the use of the equipment acquired with this grant and participating graduate students are listed in section 5. Finally, information about the acquired equipment is provided in section 6.

I. INTRODUCTION

In-situ real time monitoring of chemical and physical changes during processing of reactive materials, polymer-forming and non polymer-forming alike, is of crucial importance to scientists and engineers engaged in efforts to optimize processes and products in various industries, from chemical and pharmaceutical to electronic and aerospace. Information collected in-situ by sensors is transmitted in real time to the process computer whose task is to control the system parameters by taking corrective actions without the need to examine the output streams and thus to guide the process along an optimum path. The principal elements of an in-situ process control loop are the signal source, the transmission line, the sensor and the detector. It is clearly desirable to operate a monitoring setup in the **remote** mode which enables one to continuously measure changes in chemical and physical properties as they occur during processing in difficult to access places, such as dies, molds, reactors or autoclaves, which operate in the presence of various aggressive environments.

Fourier Transform Infrared Spectroscopy (FTIR) represents a particularly attractive choice among various monitoring techniques, owing to the unparalleled breadth and wealth of molecular-level information contained in the infrared portion of the electromagnetic spectrum. But while the use of conventional (off-line) FTIR spectroscopy to study reactive systems has been documented in the literature, the use of remote FTIR for in-situ real time monitoring of processes has a much more recent origin. Our principal objective was to purchase components and assemble setups for remote NIR and MIR spectroscopy, and utilize them for in-situ real time studies of reactive processing.

II. REMOTE FIBER OPTIC NEAR-INFRARED SPECTROSCOPY

The infrared region is broad and the vast majority of reported studies of reactive systems have been carried out in the MIR range, which extends between about 4,000 and 400 cm^{-1} (2.5-25 μm) and is replete with fundamental absorptions. Only a handful of investigations of reactive systems have been conducted in the NIR range, which extends from about 14,000 to 4,000 cm^{-1} (0.7-2.5 μm) and which contains weaker overtones of the fundamental absorptions. But the NIR range has one major advantage over the MIR range in that it can be transmitted through silica type optical fibers which are relatively inexpensive and are readily available in a variety of types and forms. In addition, the NIR range is characterized by lower absorptivities than the MIR range and is hence conducive to measurements of thicker samples. A Nicolet Magna-IR System 750 Fourier Transform Infrared Spectrometer, with spectral range coverage from 15,800 to 50 cm^{-1} and the Vectra scanning interferometer with a better than 0.1 cm^{-1} resolution, was purchased and used. NIR data were obtained using a CaF_2 beamsplitter, a white light source and an MCT detector cooled with liquid nitrogen.

A schematic representation and a photograph of our experimental setup are shown in Figures 1 and 2, respectively.

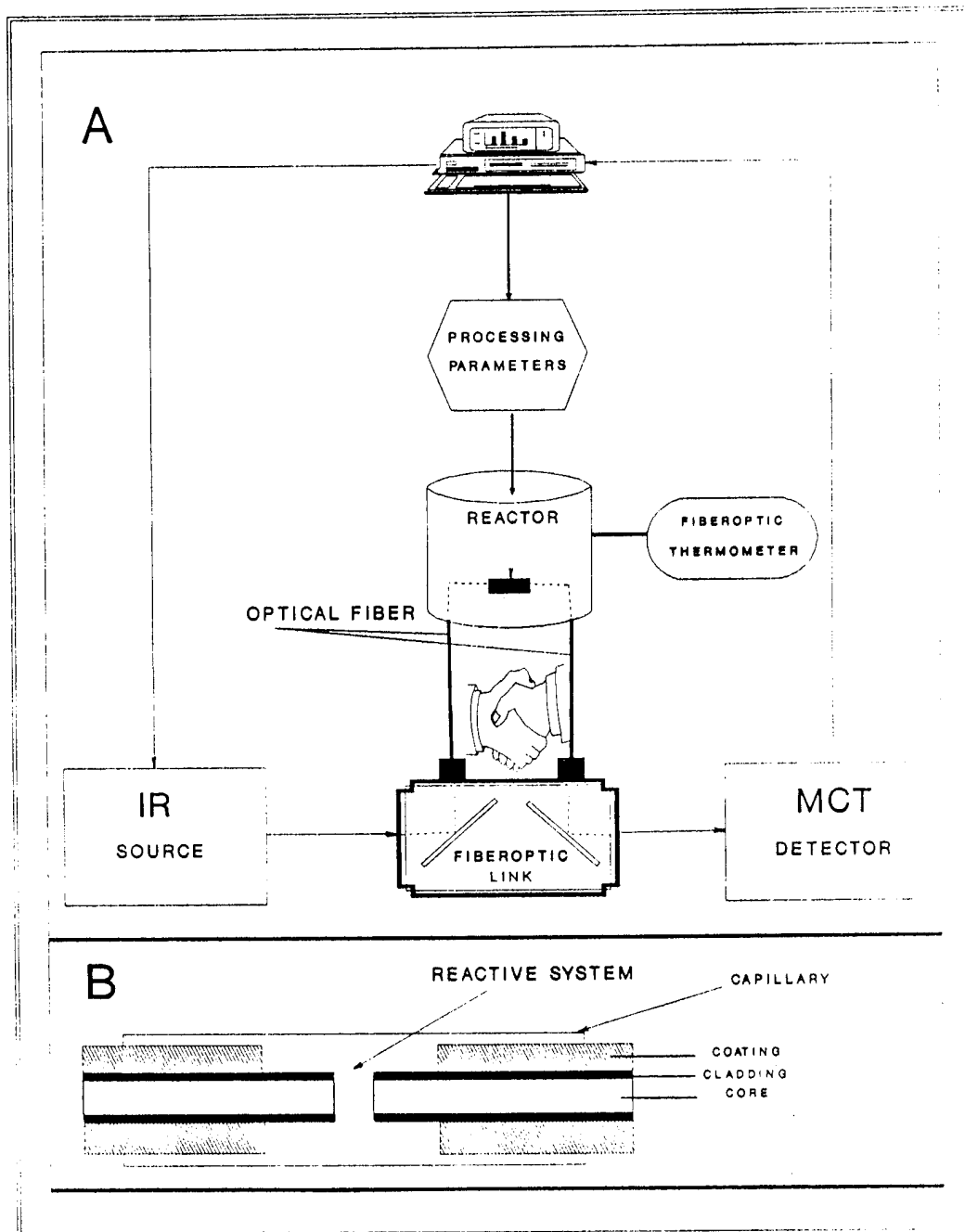


Figure 1. A. Schematic of remote fiber optic NIR spectroscopy assembly; B. Schematic of optical fiber/capillary disposable cell configuration.

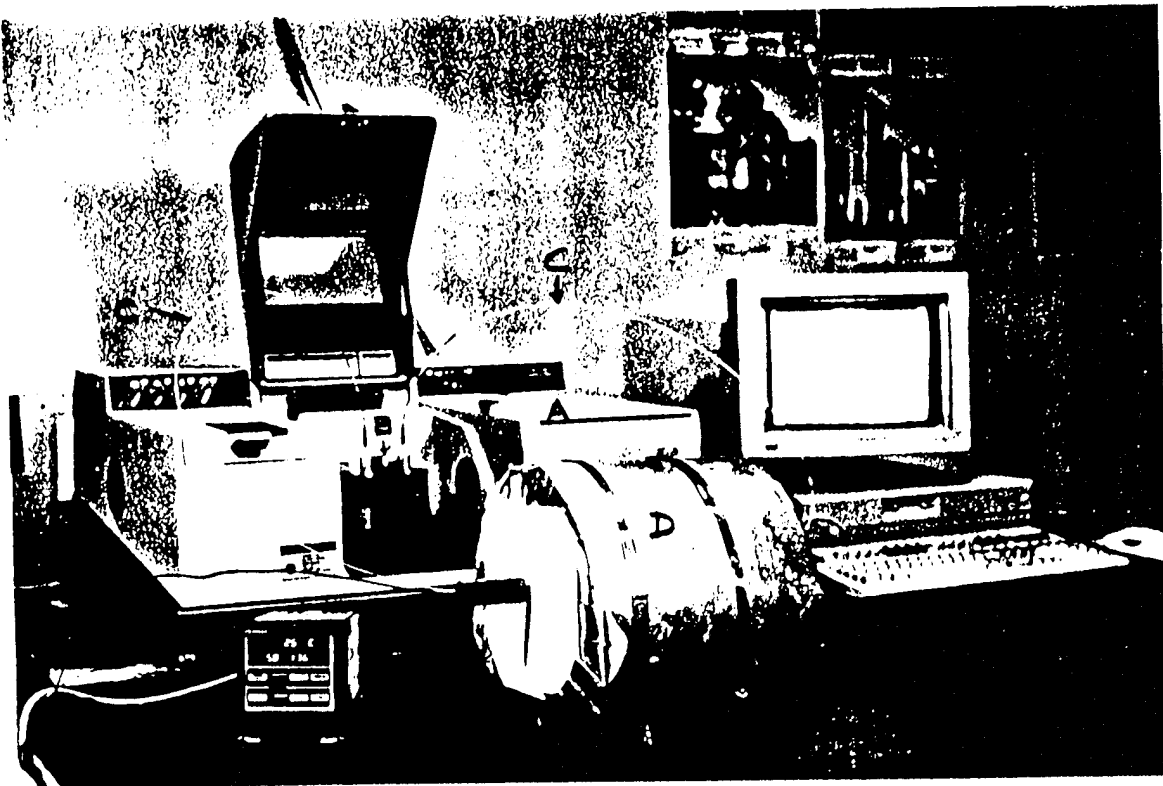


Figure 2. Photograph of remote fiber optic NIR spectroscopy assembly: A - FTIR spectrophotometer, B - fiber optic link, C - transmitting and receiving legs of the optical fiber, D - reactor, E - programmable temperature controller, F - fluoroptic thermometer.

A large core (600/630 μm) low -OH fused silica type multimode optical fiber (3 M's specialty optical fiber) was used. The fiber was characterized by attenuation at 630 nm of less than 50dB/km and a numerical aperture of 0.39 \pm 0.02. Two lengths of the fiber (lengths of up to 10 meters were successfully tested) were utilized as receiving and transmitting legs. An optical fiber link containing reflective mirrors was used to couple the signal into the transmitting and out of the receiving leg. SMA connectors (Newark Electronics) were utilized to attach fiber legs to the fiber link. At the sample side, two distal fiber ends were axially centered and positioned to face each other. Depending on the type and size of sample, several disposable cell configurations were designed and successfully tested. All had an adjustable path length, enabling us to optimize the signal. In most instances, a pathlength of 2-3 mm was sufficient for excellent transmission and a clear NIR absorption signal down to 4,000 cm^{-1} . The results shown in this column were generated using the optical fiber/capillary configuration, schematically shown in Figure 1B. A short length (less than 10 mm) of protective buffer was removed from the distal ends of transmitting and receiving fiber legs, which were then slipped into the capillary to a desired pathlength. The space between fiber ends was filled with the reactive mixture free of bubbles and the whole assembly was inserted into a programmable temperature controlled chamber. A highly accurate measurement of the sample temperature is essential in kinetic studies, and that places a premium on the experimental precision. Temperature during reaction was monitored with Luxtron's 750 Multichannel Fluoroptic Thermometer, by placing the tip of its optical fiber probe in direct contact with the portion of capillary filled with the reactive mixture.

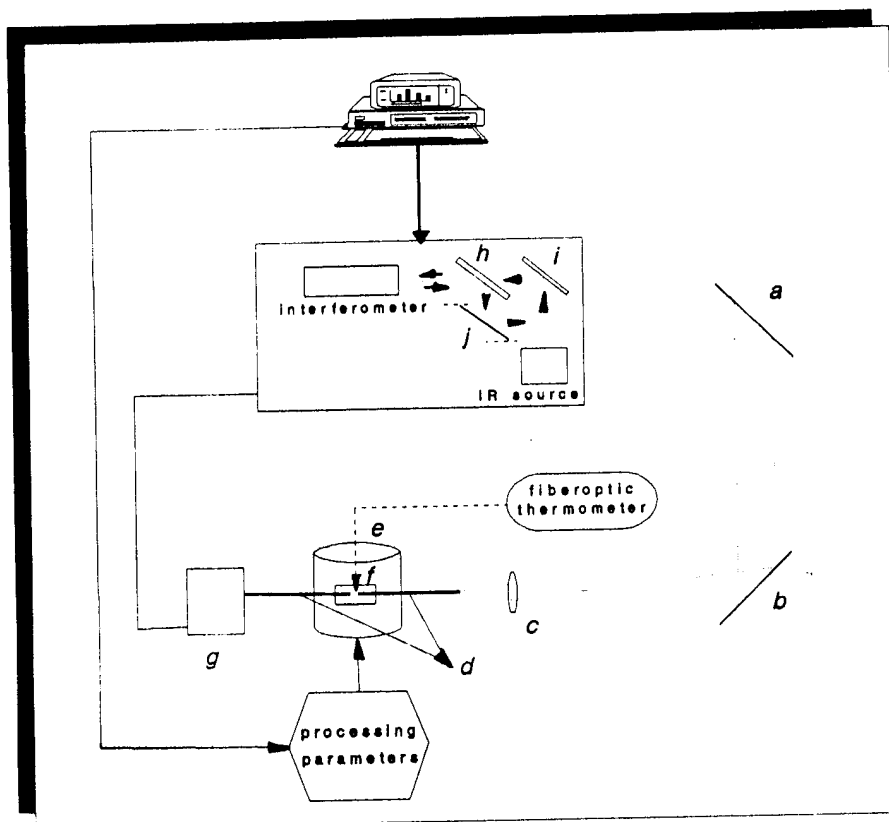
The above described experimental procedure is very attractive; it features a simple design, low cost,

small sample size, short preparation time, in-situ real time response and remarkable reproducibility and reliability of data. Most importantly, however, the cell is disposable, in contrast to several recently marketed and quite expensive commercial fiber optic probes (e.g. Nicolet/Spectra Tech, Axiom, Guided Wave) that are non-disposable and hence cannot be used to monitor processing of thermoset polymers and composites. After curing of our sample, a small length of the optical fiber embedded in the cured resin is cleaved and the new ends polished to a clean mirror-flat surface for the next run.

III. REMOTE MID-INFRARED SPECTROSCOPY

In the MIR range, which extends between about 4,000 and 400 cm^{-1} (2.5-25 μm) and is replete with fundamental absorptions, only costly and exotic state-of-the-art chalcogenide and metal halide fibers have the required transmission capabilities, and even then usually over a limited frequency interval. Thus a novel approach had to be undertaken.

Naturally, the same spectrophotometer was used. MIR data in the 4,000 to 600 cm^{-1} range were collected using an IR source, KBr beamsplitter and a MCT detector, which was cooled with liquid nitrogen before each run. All spectra were obtained at 4 cm^{-1} resolution using 100 scans. Schematic presentation and a photograph of our MIR setup are shown in Figures 3 and 4, respectively.



LEGEND :

- a gold coated first surface flat mirror
- b gold coated focusing mirror (focal length = 760mm)
- c ZnSe positive meniscus lens (focal length = 62.5mm)
- d nickel tubes (1 foot each, I.D. 1/16", gold coated inside)
with NaCl windows (d=6mm,thickness=1mm) bonded on each end
- e reactor
- f reaction vessel
- g MCT (liquid nitrogen cooled) detector
- h beamsplitter
- i parabolic mirror
- j sliding mirror

Figure 3. Schematic of experimental setup for remote MIR spectroscopy

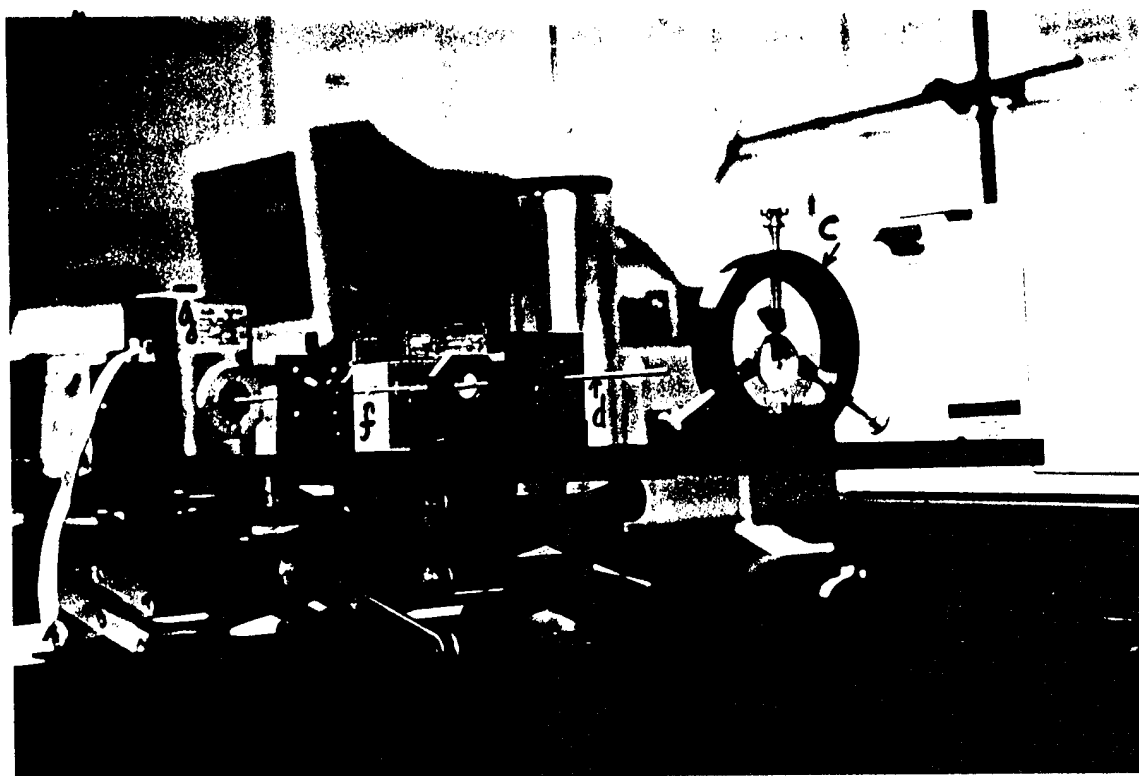
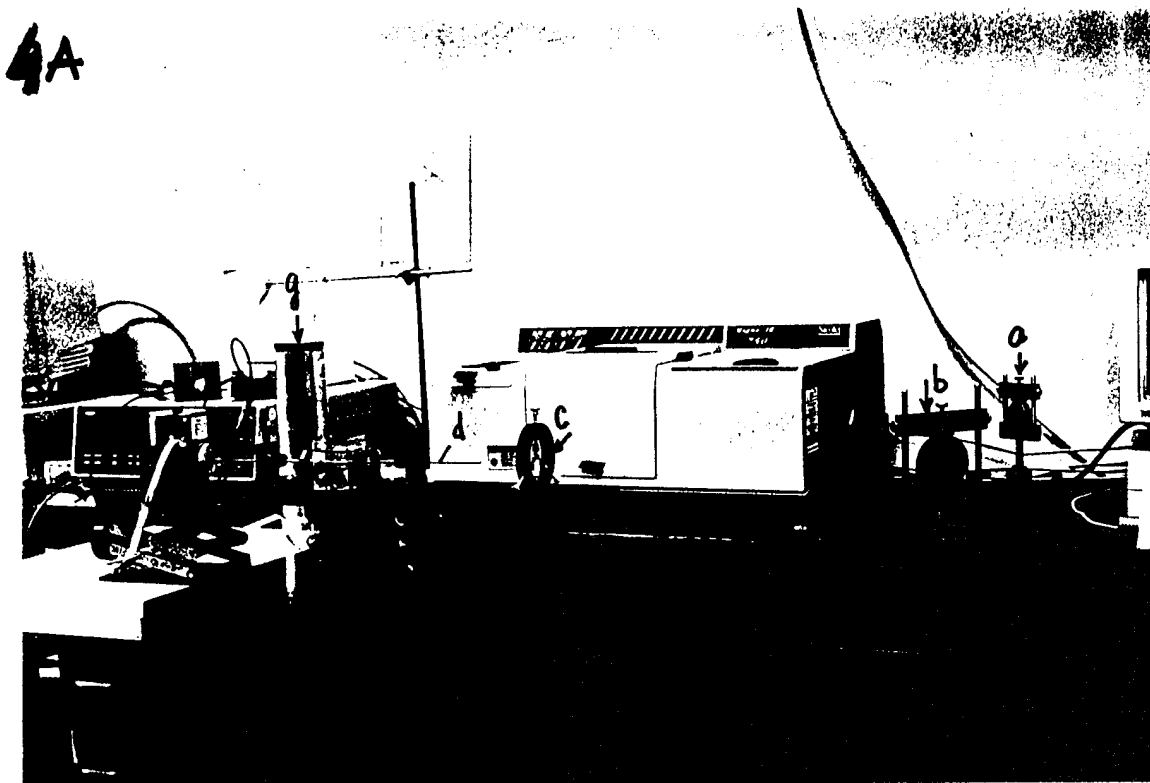


Figure 4. Two views of remote MIR setup. Letters correspond to those in Figure 3.

In order to conduct remote MIR measurements, the IR beam had first to be directed out of the instrument. This was accomplished by placing a sliding mirror inside the optical bench compartment in the path of the beam near the exit from the interferometer. The sliding mirror is controlled by the computer and it can redirect the beam through the external ports on either side of the optical bench. Next, a series of optical components (for details see the legend in Figure 3) was used to advance the beam a desired distance and focus it into a hollow nickel waveguide. The waveguide had an inside diameter of 1,56 mm and was 30 cm long. The inside was coated with gold, a highly reflective IR substance. Two identical waveguides were employed as receiving and transmitting legs. The waveguides were inserted into the reaction mixture through the holes drilled in the sides of the reaction vessel. A pair of NaCl windows (6mm in diameter, 1mm thick) were attached to the end of each waveguide. The incoming IR beam advances down the receiving waveguide by internal reflection, travels through the sample where it collects the spectral information, and then proceeds down the transmitting waveguide by internal reflection towards the detector. The distance between the NaCl windows, and hence the sample thickness, is adjustable. Under the conditions of this study, the optimum absorption was obtained with a pathlength between 200 and 500 μ m. MCT detector was removed from the optical bench compartment and placed immediately adjacent to the far end of the transmitting leg to minimize the loss of signal which was then processed by the FTIR computer.

Two different disposable reaction vessels were used initially; polypropylene vessels (32x25x 20mm) for reaction temperatures up to approximately 130°C, and aluminum vessels for higher temperature. Heating was accomplished by wrapping a rubber extruded heating tape around the reaction vessel. Temperature calibration was performed on non-reactive systems using Luxtron's 750 multichannel

fluoroptic thermometer. The fiber optic probe was immersed in the sample and its tip placed in the immediate vicinity of the space between the two NaCl windows. Stable isothermal conditions were achieved for all runs at all times. By maintaining the reaction vessel at cure temperature before injecting the sample we were able to minimize the time lag due to conduction while reaching the processing temperature. A fine gage Omega thermocouple was placed inside the sample to record the temperature during cure. Upon the completion of cure a short length of the exposed end of each waveguide was cut off with jeweler's saw and the new surface polished prior to the subsequent run. We stress that the above described remote MIR setup is novel, inexpensive, versatile, and of potentially broad appeal since it can be utilized to generate in-situ real time MIR spectra in conjunction with practically any reactor and/or operating environment.

IV. SELECTED RESULTS OBTAINED WITH REMOTE NIR AND MIR SPECTROSCOPY

Examples of results were selected from non polymer-forming epoxy/amine model system and a series of multifunctional epoxy/amine. All reactants were mixed in stoichiometric proportions and tested under isothermal conditions.

Examples of results of **remote NIR spectroscopy** are shown first. In Figures 5 and 6 we show series of spectra (shifted along the ordinate for clarity) obtained with our fiber optic probe during phenyl glycidyl ether (PGE)/aniline (non polymer-forming system) reaction at 110°C and diglycidyl ether of bisphenol A/ 1,8 diamino naphthalene, or DGEBA/DAN, (polymer-forming) reaction at 100°C, respectively.

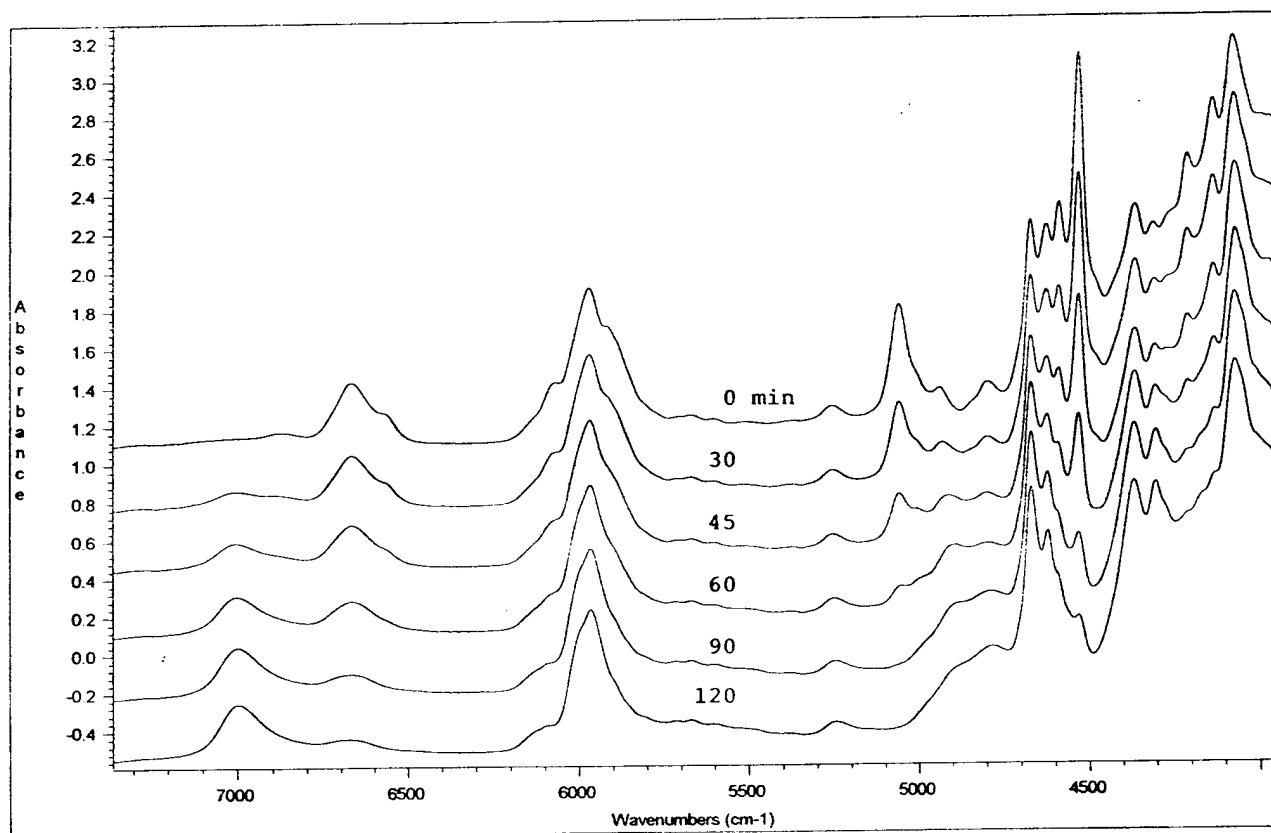


Figure 5. NIR spectra of PGE/aniline system during reaction at 110°C, with reaction time in minutes as a parameter.

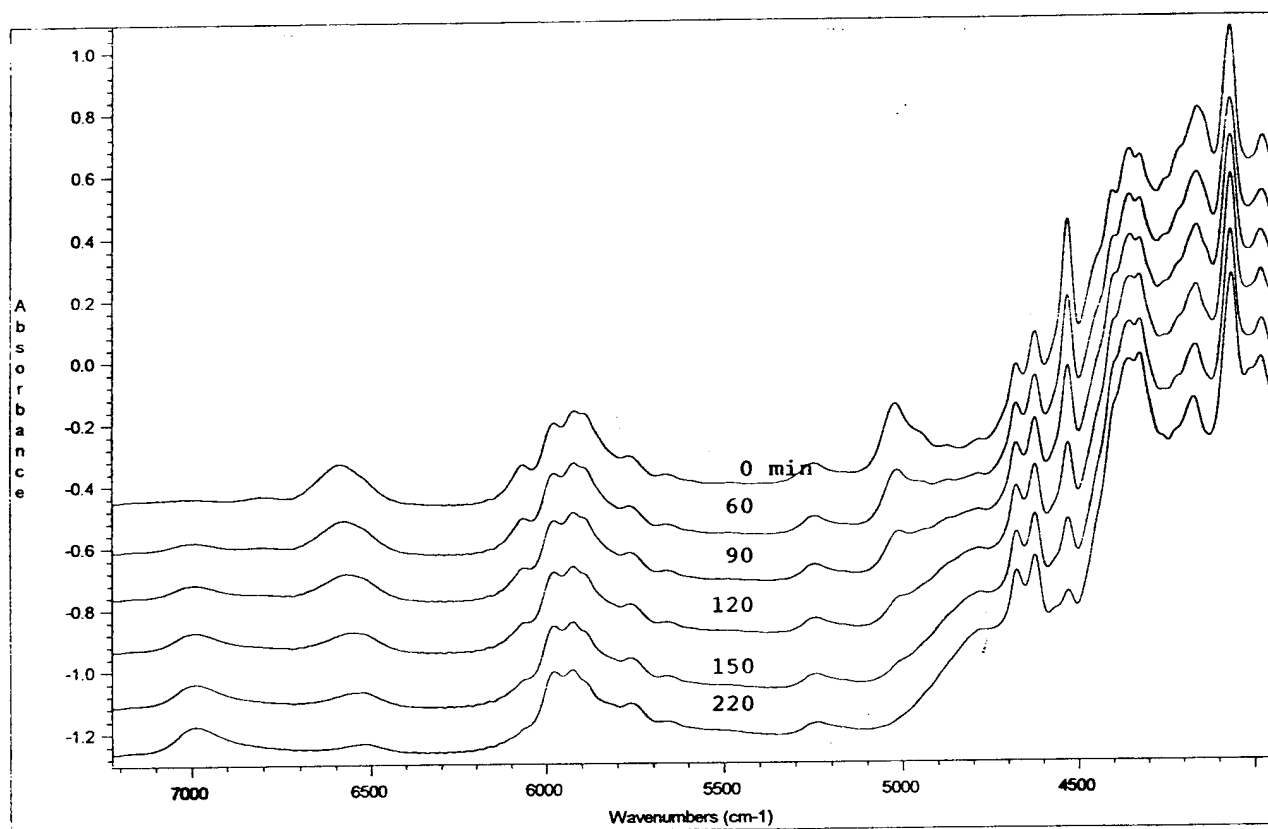


Figure 6. NIR spectra of DGEBA/1,8 DAN system during reaction at 100°C, with reaction time in minutes as a parameter.

Spectra are very "clean", free of noise, completely reproducible, with sharp peaks, and in every aspect as good as those obtained by conventional FTIR spectroscopy. The progressive changes in spectra were systematic and conducive to precise quantitative analysis. The trends displayed by major peaks of relevance in epoxy/amine reactions were evident; a decrease in epoxy absorption (4,530 and 6,080 cm^{-1}), a decrease in amine absorption (5,000 and 6,670 cm^{-1}), and an increase in hydroxyl absorption (7,000 and 4,800-4,900 cm^{-1}). Spectral data of the type shown in Figures 5 and 6 can be used for quantitative determination of reaction kinetics. In the studies of epoxy cure it is convenient to calculate the extent of reaction(α) at any time t from the initial areas of epoxy and reference peaks, $A_{\text{epoxy},0}$ and $A_{\text{ref},0}$, respectively, and their corresponding values at time t , $A_{\text{epoxy},t}$ and $A_{\text{ref},t}$ according to the following equation:

$$\alpha = 1 - [(A_{\text{epoxy},t})(A_{\text{ref},0})]/[(A_{\text{epoxy},0})(A_{\text{ref},t})] \quad (1)$$

Here, the peak at 4,530 cm^{-1} was used to monitor the disappearance of epoxy groups. Various reference peaks were examined and the most reproducible results were obtained using the peak due to the C-H stretching vibration of the benzene ring at 4,673 cm^{-1} . An example of quantitative kinetic results is shown in Figure 7, where the extent of reaction of DGEBA/DAN multifunctional formulation, calculated from equation 1, is plotted as a function of reaction time with reaction temperature as a parameter. Another interesting example is shown in Figure 8, which depicts extent of reaction as a function of reaction time at 98°C for a series of multifunctional epoxy/amine formulations.

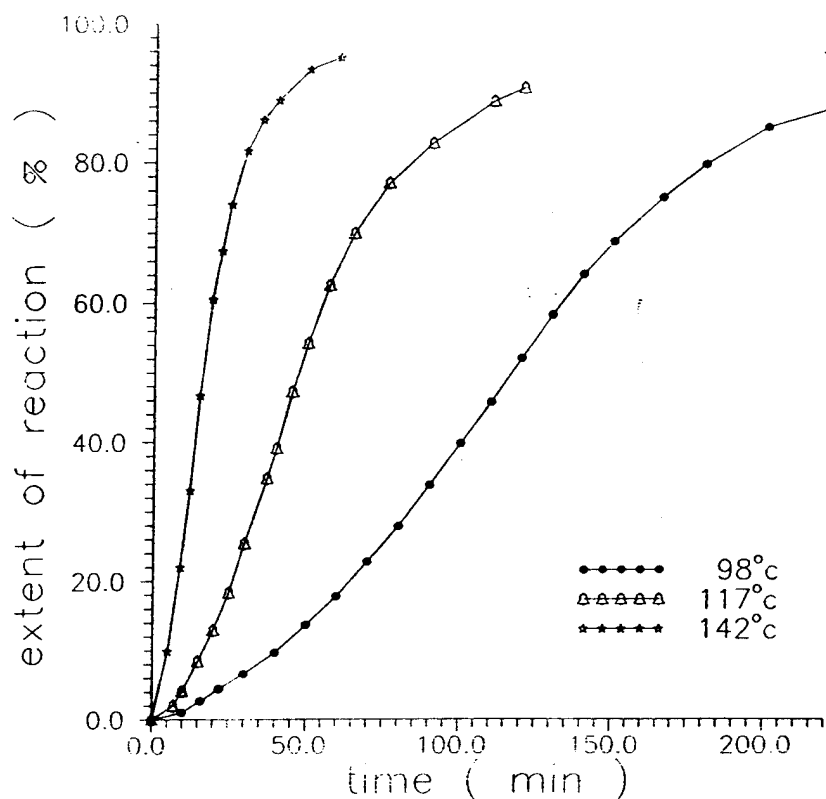


Figure 7. Extent of reaction of DGEBA/1,8 DAN system as a function of reaction time, with temperature as a parameter.

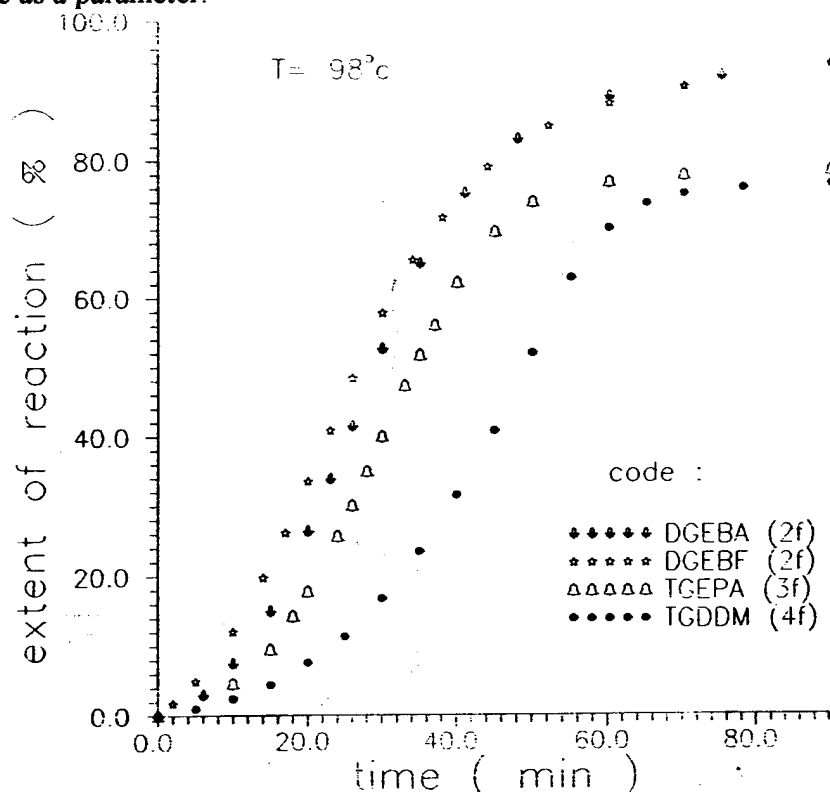


Figure 8. Extent of reaction of DGEBA/MDA, DGEBF/MDA, TGEPA/MDA and TGDDM/MDA formulations as a function of reaction time at 98°C.

Each formulation contained the stoichiometric ratio of 4,4' methylene dianiline (MDA) and one of the following epoxy resins: diglycidyl ether of bisphenol F (DGEBF), diglycidyl ether of bisphenol A (DGEBA), triglycidyl ether of para-aminophenol (TGEPA), and tetraglycidyl 4,4' diaminodiphenyl methane (TGDDM). An examination of the results reveals the effect of molecular architecture of epoxy molecule on the reaction kinetics.

As an example of the use of **remote MIR spectroscopy**, we show our results for a multifunctional epoxy/amine formulation composed of diglycidyl ether of bisphenol F (DGEBF) and 4,4' methylene dianiline (MDA). The peak at 915 cm^{-1} was used to measure the disappearance of the epoxy group. An enlarged view of the epoxy absorption region between 970 and 915 cm^{-1} is shown in Figure 9.

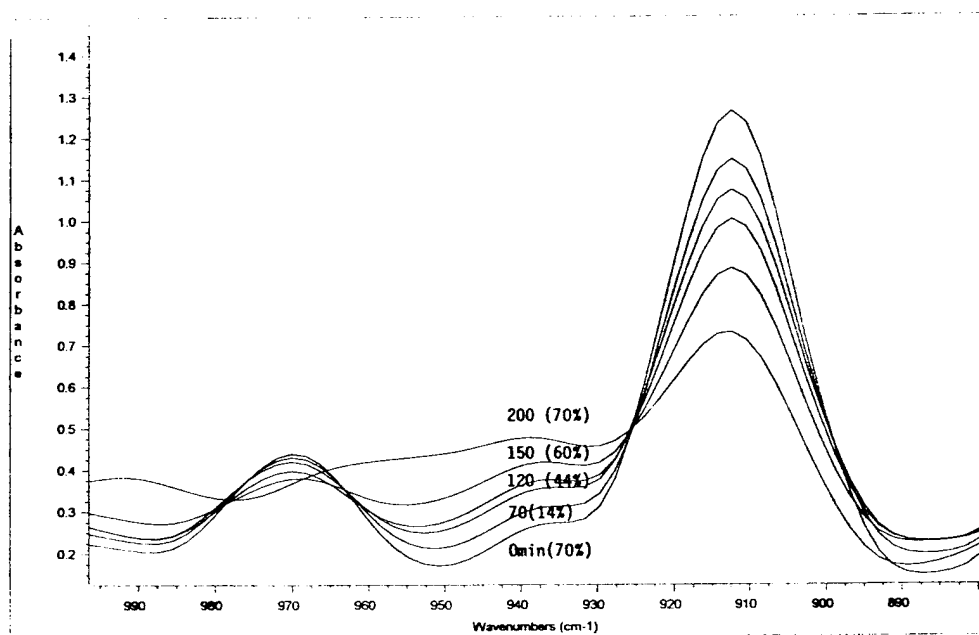


Figure 9. Enlarged view of changes in epoxy absorption peaks at 970 and 915 cm^{-1} during 200 minutes of DGEBF/MDA cure at 73°C .

For kinetic calculations, various reference peaks were examined and the most reproducible results were obtained using the peak at $2,920\text{ cm}^{-1}$ due to the $-\text{CH}_2$ stretching vibration. The extent of reaction at 73, 86 and 100°C (calculated from equation 1) is plotted as a function of reaction time in Figure 10.

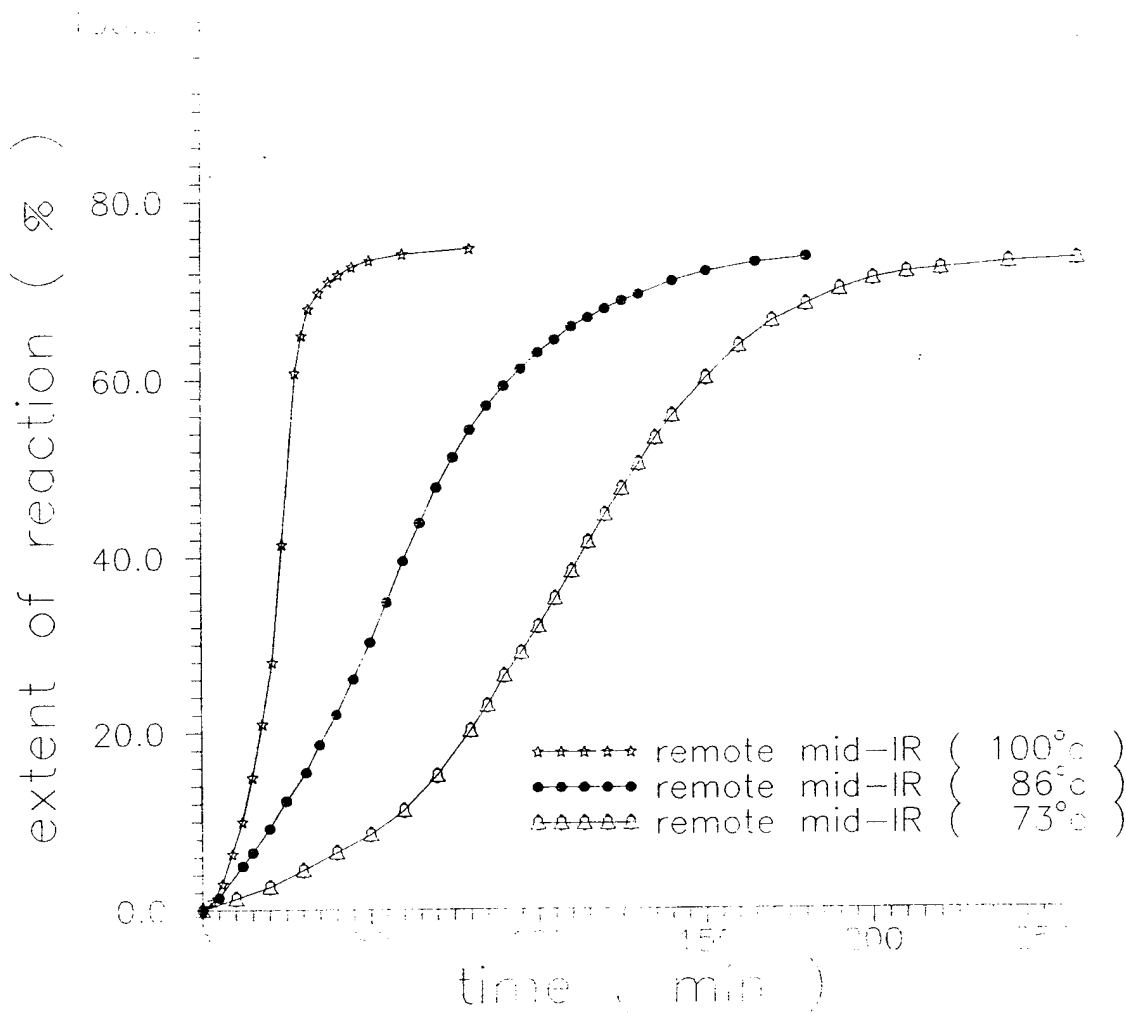


Figure 10. Extent of reaction of DGEBA/MDA formulation as a function of cure time with cure temperature as a parameter.

In conclusion, we are pleased to report that experimental setups for in situ real time process monitoring by remote NIR and MIR spectroscopy are now available in our laboratory. Investigation of polymer forming systems was made possible by designing and utilizing a disposable sample cell. The results were characterized by a strong, clean signal and superb reproducibility. Both setups are relatively inexpensive, and can be adjusted for use with practically any processing vessel and/or operating conditions. We believe that remote NIR and MIR spectroscopies are bound to become the foremost diagnostic tool for in-situ real time monitoring in the processing industry.

V. PUBLICATIONS AND PARTICIPATING STUDENTS

Publications

1. Mijovic,J., and Andjelic,S., "A Study of Reaction Kinetics by Near-Infrared Spectroscopy. 1. A Comprehensive Analysis of Model Epoxy/Amine System", *Macromolecules*, 28, 2787 (1995).
2. Mijovic,J., Andjelic,S., Yee,C.Y.W., Bellucci,F., and Nicolais,L., "A Study of Reaction Kinetics by Near-Infrared Spectroscopy. 2. "Comparison with Dielectric Spectroscopy of Model and Multifunctional Epoxy/Amine Systems", *Macromolecules*, 28, 2797 (1995).
3. Bellucci,F.,Nicolais,L., and Mijovic,J., "Impedance Spectroscopy of Reactive Polymers. Correlations with Gelation and Vitrification", *J.Electrochem.Soc.*, 142 (4), 1176 (1995).
4. Mijovic,J., Andjelic,S., Fitz,B.D., Mondragon,I., Bellucci,F., and Nicolais,L., "Impedance Spectroscopy of Reactive Polymers. 3. Correlations Between Dielectric, Spectroscopic and Rheological Properties During Cure of a Trifunctional Epoxy Resin ", submitted for publication to *J.Polym.Sci.,Polym.Phys.Ed.*
5. Mijovic,J., and Andjelic,S., "In-Situ Real Time Monitoring of Reactive Systems by Remote Fiber Optic Near-Infrared Spectroscopy", *Polymer*, in press.
6. Mijovic,J., and Andjelic,S., "Monitoring of Reactive Processing by Remote Mid-Infrared Spectroscopy", submitted for publication in *Polymer*.

7. Mijovic,J., and Andjelic,S., "Novel Research Trends 2. In-Situ Real Time Monitoring of Reactive Systems by Remote Fiber Optic Near-Infrared Spectroscopy", Polymer News, in press.

8. Mijovic,J., and Andjelic,S., "A Study of the Mechanism and Rate of Bismaleimide Cure by In-Situ Real Time Fiber Optic Near-Infrared Spectroscopy", submitted for publication in Macromolecules.

Participating Graduate Students

1. C.Y.W.Yee, MS in Chemical Engineering, May 1994 (currently with DOE, Bismarck, SC)
2. S.Andjelic, MS in Polymer Science and Engineering, April 1995.
- 3.S.Andjelic, PhD in Polymer Science and Engineering, in progress.
4. B.D.Fitz, PhD in Polymer Science and Engineering, in progress.
5. W.Corso, MS in Chemical Engineering, in progress.

VI. ACQUIRED EQUIPMENT

The equipment actually acquired is described below. Manufacturers are stated and costs rounded off. Spectrophotometer (Nicolet, \$32,000); Spectrophotometer - Near IR option (Nicolet, \$6,000); MCT detector (Nicolet, \$7,000); Work station and peripherals (Nicolet, \$5,000); Advanced software, data acquisition (Nicolet, \$8,000); ATR accessory (Nicolet \$2,000); Heated Cell (Nicolet-Spectra Tech, \$800); remote NIR accessories (various manufacturers: optical fibers, connectors, links etc. \$4,500); remote MIR accessories (various manufacturers: optical mirrors, lenses, gold-coated waveguides etc. \$ 4,500). Various pieces of equipment were extensively tested prior to their purchase and that's why an extension was requested and granted.